LIFETIME TESTING OF CATALYSTS FOR CONDITIONING THE PRODUCTS OF A BIOMASS GASIFIER

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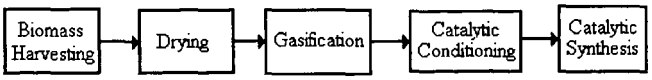
INTRODUCTION

The National Renewable Energy Laboratory, in collaboration with its industrial and academic partners, is engaged in a project with the goal of developing and facilitating the commercialization of safe, cost-effective, and environmentally benign technologies for the production of transportation fuels from biomass via thermal gasification. The block diagram below illustrates the steps involved.



The research presented in this paper focuses on the catalytic conditioning step, also referred to as hot-gas conditioning. The product of biomass gasification is crude synthesis gas, a mixture of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), steam, and higher molecular weight hydrocarbons and oxygenates (referred to as tar). The goals of synthesis gas conditioning are threefold: 1) reduce the concentration of tar by catalyzing steam reforming reactions; 2) reduce the concentration of methane by catalyzing steam reforming reactions; 3) increase the hydrogen/carbon monoxide ratio from the value of 0.7 (representative of crude syngas from a biomass gasifier) to about 2 (desirable for production of synfuels or H_2) by catalyzing the water-gas shift reaction.

Previous investigations have focused on developing catalysts or disposable solids to achieve hot-gas conditioning. The most promising materials identified in recent work have been commercial supported nickel (Ni)-steam reforming catalysts and dolomite.[1-7] Dolomite is only moderately effective for tar destruction. The primary issue with Ni-based steam reforming catalysts is lifetime. When exposed to the high molecular weight aromatic hydrocarbon and oxygenated compounds found in biomass gasifier tar, supported Ni catalysts deactivate on a time scale that is unacceptable for commercial use.

EXPERIMENTAL METHODS

The experimental apparatus is illustrated in Figure 1. It includes a vaporizer enclosed in a single zone furnace. A high pressure, positive displacement liquid pump feeds water to the vaporizer for steam generation. A second identical pump supplies a mixture of aromatics (benzene, toluene, and naphthalene) to simulate the tar found in syngas from a biomass gasifier. The liquids are vaporized in a stainless steel tube packed with stainless steel balls. Hydrogen and a 3:1:1 mixture of CO, CO_2 and CH_4, are also metered into the vaporizer through mass flow controllers. This model crude syngas solution is fed into a catalytic reactor operating in down-flow mode and heated by a three zone furnace equipped with microprocessor temperature control. Reactors are fabricated from stainless steel with aspect ratios appropriate for catalyst loads between 0.5 grams and 30 grams. Catalyst particles are ground and sieved to 16-20 mesh size (0.841 mm to 1.19 mm). Two basic reactor/catalyst configurations are tested, a commercial Ni-based steam reforming catalyst alone and Ni catalyst in conjunction with an upstream high-temperature water-gas shift co-catalyst in a dual bed reactor. The Ni catalysts are reduced overnight (15 hrs) prior to use in a stream of 14% H_2 in steam and He at 600°C. The composition of the feed and product mixtures is monitored by two computer controlled, on-line gas chromatographs; one for the permanent gases (Carle Refinery gas analyzer) and one for tar (Hewlett Packard 5890II with a DB-5 capillary column). The apparatus is automated and equipped with safety features that allow it to operate unattended during extended lifetime tests.

RESULTS AND DISCUSSION

Supported Ni catalysts will catalyze steam reforming of methane and tar compounds. Figure 2 illustrates the performance of United Catalysts Inc. (UCI) G90B Ni catalyst in treating the model crude syngas mixture with a steam mole fraction of 0.5. The simulated tar solution introduced into the vaporizer was comprised of 5 mole percent naphthalene in benzene. The composition of the effluent gas was monitored hourly. The observations reported were made under steady state conditions more than 60 hours into the run. We observed near complete conversion of tar and a high conversion of methane by steam reforming; however, the effluent mixture did not achieve equilibrium with respect to water-gas shift and CO hydrogenation.

The issue of catalyst lifetime was addressed during a subsequent experiment run under similar conditions. The UCI G90B remained active for 585 hours (the experiment was stopped at this time when a feed line plugged). A significant build up of coke was observed in and around the catalyst bed and many of the catalyst particles had been reduced to a fine powder. The steam content of the syngas produced during biomass gasification can be as low as 0.3-mole fraction[1], therefore the performance of the catalyst at lower steam to carbon ratios is of interest. Figure 3 shows that reducing the steam mole fraction in the feed

shortens catalyst lifetime. Thus, the use of supported nickel catalyst alone may not be practical for the synthesis gas conditioning application.[2-4] In all cases in Figure 2, steam is in excess over that required by stoichiometry for both steam reforming of tar and the water-gas shift reaction. The large effect of steam concentration in this case supports previous assertions that the water adsorption rate is important for these reactions.[8]

Alumina will catalyze the water-gas shift reaction at high temperatures[9]. Figure 4 illustrates this activity for χ-alumina at 815°C. Near equilibrium concentrations of CO, H_2, and CO_2 were observed with and without steam pretreatment (50% steam in He for 10 hours at 850°C) and in the presence and abscene of a model tar compound (1 mole percent toluene). In separate experiments, an η-alumina also catalyzed the water-gas shift reaction. Coke was not formed to a significant extent on either of the aluminas.

The combined effect of the alumina and nickel catalyst would fulfill the syngas conditioning objectives if their performance characteristics were additive. Figure 5 shows the results of an experiment addressing this possibility. The primary bed containing Imperial Chemical Industries (ICI) 46-1, K-promoted supported Ni catalyst was combined with an upstream co-catalyst bed of χ-alumina. The ICI catalyst was used in this initial proof of concept run because it has been shown to be active for conditioning of the effluent of a biomass gasifier and is resistant to deactivation.[10] Later experiments involved UCI G90B because it was expected that this catalyst would be more susceptible to deactivation in this application, increasing the sensitivity of investigation of the efficacy of the alumina bed.[11] This dual bed reactor was fed with a model crude syngas mixture containing a 0.5-mole fraction steam and a 0.01-mole fraction toluene. Figure 5 shows that both toluene and methane steam reforming and water-gas shift are achieved simultaneously. Thus, the dual bed concept provides the catalyst activity needed to effectively condition biomass gasifier synthesis gas, but questions of catalyst lifetime remain.

The function of the upstream, co-catalyst bed is to catalyze the water-gas shift reaction. This is postulated to improve the lifetime of the downstream Ni steam reforming catalyst by increasing the concentration of hydrogen adsorbed on the surface of the Ni crystallites. An increased surface hydrogen atom coverage could inhibit coke formation if the rate of hydrogenating adsorbed coke precursors is greater than the rate of precursor polymerization. Table 1 outlines a 2^4 factorial designed to test this hypothesis. The primary response is the elapsed time until the "end of useful life". This transition corresponds to a loss of tar and methane reforming activity, i.e., when gas chromatographic peak areas for methane and tar compounds rose to within experimental error of the areas of the same peaks during control runs.

Table 1 also summarizes the results of the 2^2 factorial subset of this experimental work that has been completed to date. In this work, the model crude syngas mixture contained 0.3-mole fraction steam and a 0.03-mole fraction of tar solution comprised of 5 mole percent naphthalene in benzene. Based on the results of previous work, the total gas flow rates and the amounts of UCI G90B and alumina were chosen to give a gas hourly space velocity (GHSV) of 170,000 h^{-1} for the Ni catalyst, and a GHSV = 2,000 h^{-1} for the alumina catalyst. The response reported for the 2^2 factorial experiment is the loss of tar reforming activity. In some cases, the loss methane of reforming activity occurred more quickly than the loss of tar reforming activity, but our conclusions regarding the use of the alumina co-catalyst bed are not altered.

This 2^2 experimental design investigated the main effects of the presence or absence of an upstream alumina co-catalyst bed and the temperature of the reactor. It shows that the co-catalyst bed significantly increases the lifetime of the Ni catalyst (B = +55 hours). Figure 6 illustrates this effect; increased lifetime was observed with respect to methane, benzene, and naphthalene steam reforming. Data analysis also revealed that the temperature and temperature-co-catalyst interaction are less important (T = +13 hours and B x T = +23 hours). When the entire 2^4 design matrix has been completed, it will be possible to estimate the standard error in the response based on the magnitude of third and fourth order interactions and tests of significance will be performed.

CONCLUSIONS AND FUTURE WORK

Our results show that a dual bed configuration using alumina as a co-catalyst upstream of a conventional Ni-based steam reforming catalyst provides appropriate activity and can increase the catalyst lifetime for catalytic conditioning of a model biomass gasifier product gas. The full experimental design also addresses main effects and interactions involving steam mole fraction and reactor temperature, as well as a comparison of the UCI G90B catalyst and an experimental catalyst (Ni/Al_2O_3 promoted with oxides of chromium, magnesium, and lanthanum). The results of a comprehensive catalyst characterization effort will be reported and the use of mixed metal oxides with perovskite structures as the co-catalyst are also planned. Finally, the optimal configuration identified in the laboratory experiments will be tested with syngas generated in a pilot scale biomass gasifier currently under construction at NREL.

ACKNOWLEDGEMENTS

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Table 1: 2^4 Experimental Design and Initial Results

Factors				Variable	Levels	
B	T	S	K		-	+
-	-	-	-	B = Co-catalyst Bed	no	yes
+	-	-	-	T = Temperature	750°C	800°C
-	+	-	-	S = Steam Mole Fraction	30%	40%
+	+	-	-	K = Ni Catalyst	UCI G90B	Exp.
-	-	+	-			
+	-	+	-			
-	+	+	-			
+	+	+	-			
-	-	-	+			
+	-	-	+			
-	+	-	+			
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+	+	+	+			

Initial Results: 2^2 Design

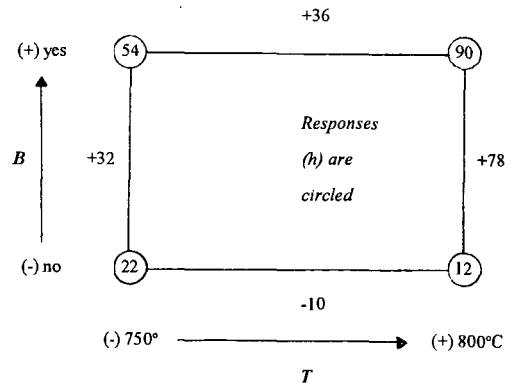

Figure 1: Schematic of Experimental Apparatus

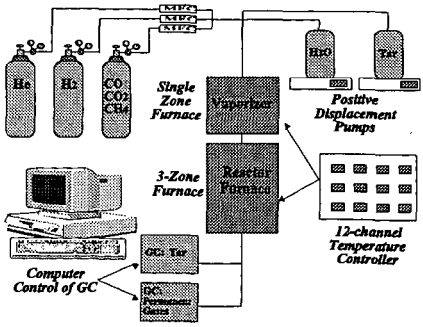

Figure 2: Activity of UCI G90B Catalyst

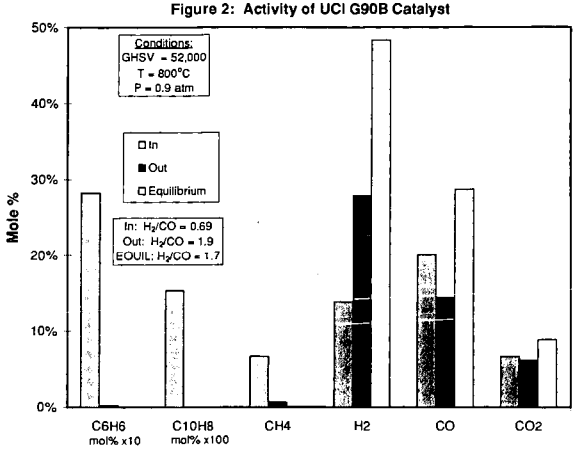

Figure 3: Effect of Steam on Time to Complete Deactivation for UCI G90B

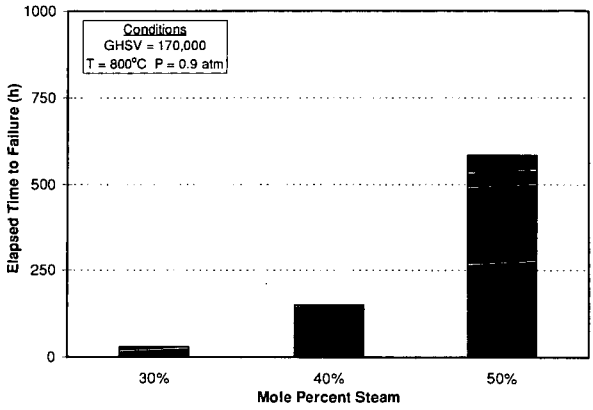

Figure 4: Water Gas Shift Activity of χ-Alumina Catalyst

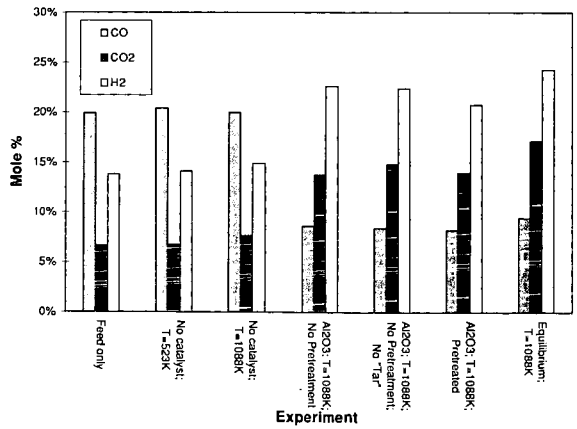

Figure 5: Activity of Dual Bed System with ICI 46-1 and χ-Al_2O_3

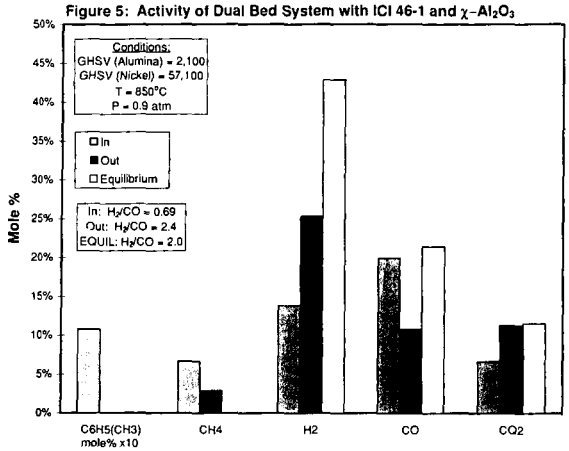

Figure 6: Steam Reforming Activity vs. Elapsed Time